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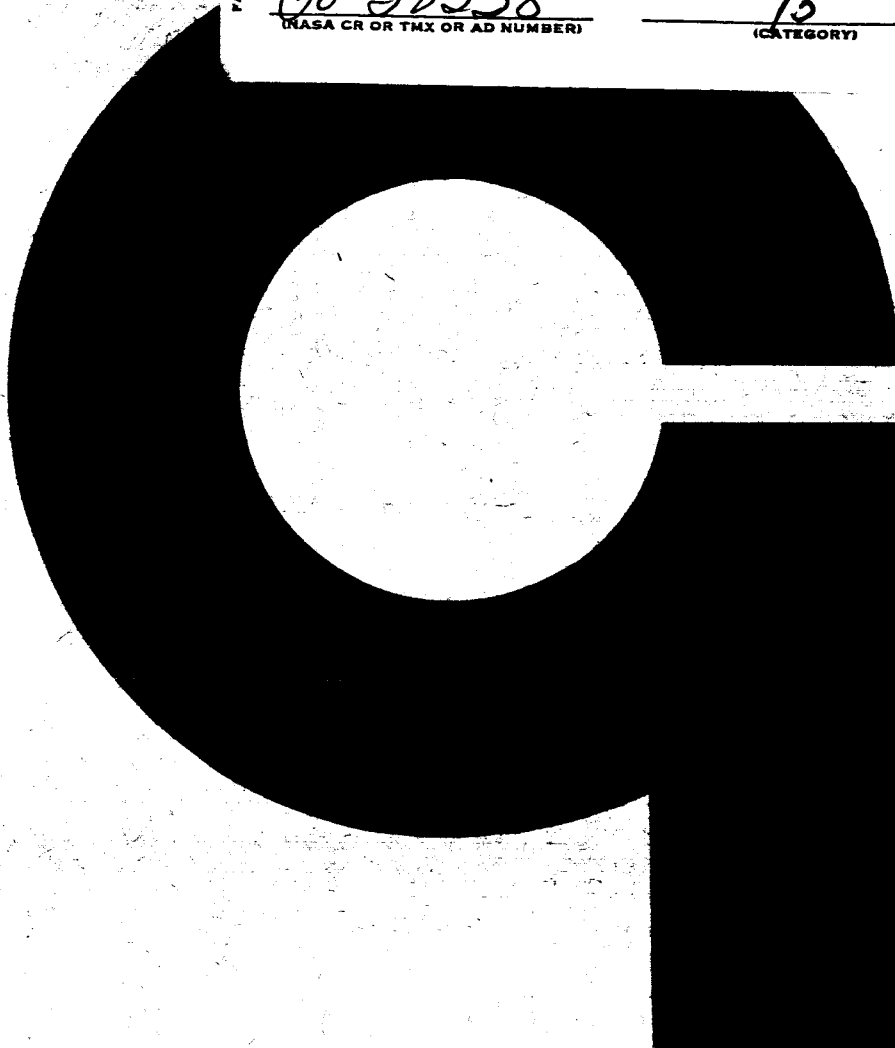
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SOLIDS MASS SPECTROMETER
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SOLIDS MASS SPECTROMETER

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During the second quarter of the contract period, a significant improvement in the instrumental background was achieved. The introduction of a zeolite trap makes it possible to eliminate undesirable noise from the sputter-ion pumps and at the same time to maintain a pressure below 10^{-7} torr in the analyser section.

In order to determine the sensitivity of the instrument for trace impurities, a series of improved spectroscopic standards has been devised.

Experimental tests have shown that impurity levels in the part per million range can be detected, even under unfavorable conditions. For the determination of statistically varying signals, as might be obtained from samples containing an inhomogeneous concentration of impurities, a digital electronic memory device has shown promising results.

Author

I. BACKGROUND

As reported previously, operation of the sputter-ion pumps gave rise to noise in the multiplier of the mass analyser. The only remedy was to shut-off these pumps during a run; this, in turn, however, caused an undesirable pressure increase in the analyser section, which ultimately resulted in malfunctioning of the multiplier.

In order to obtain adequate pumping during runs without electrical interference, a zeolite sorption pump was constructed with two parts fitted with flanges profiled for bakeable copper shear-seals. One port was connected to a sputter-ion pump (15 l/sec), the other to a 1-½-inch valve with a Viton-A seat.

The combination is first evacuated by a well-trapped conventional pump to a pressure less than 10^{-4} torr. The zeolite temperature is then raised to 350°C by means of a simple immersion heater placed in the well provided as a liquid nitrogen reservoir. Evacuation continues until the pressure, with the zeolite hot, falls below 10^{-3} torr. The zeolite-pump-sputter-ion pump-combination is then valved off and disconnected from the exhaust manifold. The pressure decreases to less than 10^{-5} torr when the zeolite cools to room temperature, and to below 10^{-7} torr when chilled to liquid nitrogen temperature.

The zeolite pump is connected to the mass spectrometer analyser, but the connecting valve is not opened until the analyser section is evacuated by the other pumps (mechanical forepump, mercury-diffusion pump and 15 l/sec sputter-ion pump) to less than 10^{-6} torr.

Initially, the zeolite pump was operated at liquid nitrogen temperature, with the sputter-ion pumps shut-off during a run. As expected, the noise in the multiplier was negligible and thus the sensitivity of the machine was greatly improved. The pumping action of the zeolite pump at liquid nitrogen temperature persists for extremely long periods for all gases except hydrogen, helium and neon; it is thus entirely suitable for the heavier noble gases such as argon, krypton and xenon which are used to bombard the targets to be analysed.

It was suspected, however, that the zeolite might be effective, even at room temperature, in preventing metastable atoms produced by the discharge in the sputter-ion pump from reaching the analyser. This turned out to be the case and it is now possible to perform experiments without disconnecting the sputter-ion pump. This procedure appears to be of importance in the operation of other instruments which have to be operated in the presence of the discharge of sputter-ion pumps and, because of its simplicity can easily be adapted to other applications.

II. SPECTRA OF SOLID SAMPLES

As reported previously, the determination of the detection limit for trace impurities is seriously hampered by the complexity of the impurity content of spectrographic standards and the uncertainty in their impurity concentration. This is true for all mass spectrometers for solids and leads to difficulties in defining the sensitivity of such instruments. A measure of the detection limit can be obtained, however, by choosing a substance containing an impurity which is widely separated on the atomic mass scale from other elements and whose concentration can be determined accurately by another independent method. A good example is a doped semiconductor, such as boron-doped silicon or antimony-doped germanium.

A simplified standard can also be obtained by limiting the number of components in a conventional spectroscopic standard consisting of spectroscopically pure graphite and a measured amount of carefully chosen trace elements. Preferably, these compounds should consist of mono-isotopic elements. At no point on the atomic mass scale should their dissociation products or multiply-charged ions overlap. An examination of the periodic table shows that this condition is satisfied in the case of the elements in Group I, Group IIIA, and Group V.

Accordingly, we have ordered a boron-doped silicon sample from the Dow-Corning Corporation and also graphite standards containing concentrations of 10 ppm, 1 ppm and less than 1 ppm of the elements Li, Na, K, Cu, Rb, Ag, Cs in Group I, from the Jarrell-Ash Company.

III. EXPERIMENTAL RESULTS

In order to keep ahead of our schedule while awaiting delivery of the above simplified standards, the practical performance of the instrument for trace impurities was investigated.

(1) Gold-sample from Bell Laboratories.

This sample, provided by Dr. Ahearn, has been doped with 0.1% of platinum. Although the two elements are adjacent on the atomic mass scale, the platinum isotopes could be identified, even ^{192}Pt which has an abundance of only 0.8%. Its concentration in the gold sample was thus 8 ppm.

(2) Meteorites from the Smithsonian Physical Observatory provided by Dr. Edward Fireman

Two iron samples were to be analysed regarding their content of ^{40}K . They were bombarded with Xenon instead of Argon to avoid interference of the bombarding ions with the 40-peak of interest. Krypton has an isotope at mass 80, so that doubly charged Krypton could interfere, whereas Xenon has no isotope at mass 120, so that even triply-charged Xenon would not interfere with the measurement.

Unfortunately, it turned out that the meteorites contained large amounts of Calcium which of course occupied mass 40. A resolving power of 30,000 would be required to resolve ^{40}K and ^{40}Ca . Therefore, the conventional method of chemically separating the Potassium seems unavoidable.

A stone meteorite "Holbrook", was to be investigated with regard to the $^6\text{Li}/^7\text{Li}$ abundance. The lithium is said to be present in a mean concentration of 10 ppm. For terrestrial material, ^6Li would be present

as 1 ppm. The sample is very inhomogeneous and it turned out that the lithium peaks could be obtained only from certain small areas by moving the sample. A run was made whereby the mass adjustment was alternated between the two peaks every 30 seconds. There was no difficulty in identifying the peaks; however, the intensities fluctuated too much to make a good quantitative comparison. A novel commercial digital memory oscilloscope was tested to determine its applicability to analyses where there are large statistical variations. The results were sufficiently promising that the instrument will be rented for a period of three months to obtain more conclusive data.

IV. ABSOLUTE SENSITIVITIES

The ion yields of the pure metals listed in Table 1 were measured under bombardment with 8 kv Xenon ions and 8 kv Argon ions. A set of three (3) samples was always mounted together with one particular tantalum sample. The ion yield obtained from the tantalum sample was taken as measure for the primary beam intensity by relating the peak heights of the three samples to that of tantalum. The primary beam was kept on while changing from one sample to the next, and the samples were adjusted for maximum output.

Table 1

	8 kv Xe ⁺	8 kv Ar ⁺
Mg	20.9	107
Al	7.2	790
Fe	4.2	22.6
Co	1.5	3.2
Ni	1.68	1.8
Cu	.79	2.4
Zn	.95	3.2
Zr	.56	3.0
Nb	.09	3.7
Ag	.01	.94
Cd	.38	.11
In	1.67	5.0
Sn	.72	
Ta	1	1
Au	.006	.008
Pb	3.0	4.2

The figures in Table 1 can be used to evaluate a mass spectrum and to calculate the relative atom concentrations in the surface layer. However, it must be expected that the composition of the surface layer of an alloy will become different from the bulk material owing to the different sputtering rates of the components. Under equilibrium conditions, all components will be sputtered in proportion to their bulk concentration and the ratio of bulk to surface concentration will be proportional to the sputtering rates. Before this equilibrium condition is reached it might be expected that the relative peak heights will change; however, this effect has not been observed. It must be assumed, therefore, that the equilibrium is already reached before the first mass spectrum is recorded.

Comparison between the results obtained with Xe^+ and Ar^+ bombardment shows that, in general, the spread in the sensitivities, or the so-called discrimination factor, is smaller for the heavier bombarding ion. This can be an advantage or disadvantage for the detection of trace impurities, depending on the elements involved. For instance, the detection limit of Al-traces in Ta is much larger, if the sample is bombarded with Ar^+ instead of Xe^+ . However, for the detection of Ta-traces in Al, the use of Xe^+ will provide the higher sensitivity.

It has also been observed that use of Xe^+ increases the number and intensity of complex molecules and fragments, as well as of multiply-charged ions. This complicates the spectrum and is therefore, in general, not desirable, unless the additional peaks are needed for the identification of the material and for the calibration of the mass scale, and do not interfere with the peaks of trace components of interest.

It is expected that light bombarding masses (He^+) will have the opposite effect and will simplify the spectrum. Tests in this direction will be performed shortly.